(54) Title: METHOD FOR MEASURING THE CONCENTRATION OF WATER IN ARGON, HYDROGEN, NITROGEN AND HELIUM BY MEANS OF IONIZATION MOBILITY SPECTROMETRY
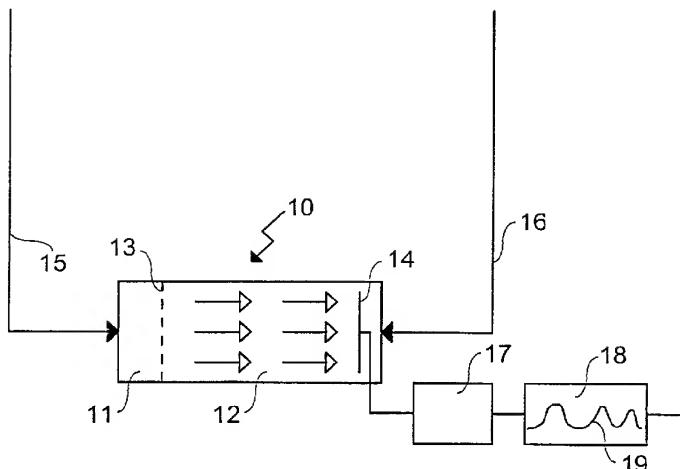
(57) Abstract: A method for measuring by means of ionization mobility spectrometry relatively high concentrations of water in argon, hydrogen, nitrogen and helium, characterized by comprising the followings operative steps: -introducing the gas to be analyzed into an IMS instrument (10) with a counter- flow of pure gas; -obtaining a signal (19) variable during the time and proportional to the number of ions detected by an ion detector (14) of the IMS instrument (10); -determining two time intervals (A, B) corresponding to the drift times in the IMS instrument (10) of the H_3O^+ and $(H_2O)_2^+$ ions; -obtaining the peaks of said signal (19) in the two determined time intervals (A, B); -calculating the water concentration in the gas to be analyzed according to the 15 ratio between the intensity of the two peaks obtained in the signal (19).

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METHOD FOR MEASURING THE CONCENTRATION OF WATER IN
ARGON, HYDROGEN, NITROGEN AND HELIUM BY MEANS OF
IONIZATION MOBILITY SPECTROMETRY

5   The present invention relates to a method for measuring the concentration of

water in argon, hydrogen, nitrogen and helium by means of ionization mobility

spectrometry.

          These gases are widely used in the semiconductor industry as transport

gases in which reactive species are diluted or as support gases for plasma

10   formation in the cathodic deposition processes (in particular, helium and argon are

employed for these uses), as well as real reagents in the process (in particular in

the case of nitrogen). Among these gases, argon is the most important for the

industry: in the rest of this text this gas will be mainly referred to, but the

invention may be also applied with the same results to the other cited gases.

15   The pureness of the argon employed in the semiconductor industry is

particularly important; as a matter of fact, contaminants which may be present in

the reagents or in the reaction environment can be incorporated into the solid state

devices, thereby altering their electrical or magnetic properties and thus leading to

production rejects.

20   The argon purification is the subject-matter of various patents, such as for

instance GB-B-2177079 (similarly, GB-B-2177080 relates to nitrogen purification

and US 5558844 and 5556603 relate to hydrogen purification). According to this

patent, argon is purified by passing it through a bed made of a getter material (an

alloy based on zirconium, vanadium and iron) kept at a temperature comprised

25   between 350 and 450 °C; alternatively, purifiers working at room temperature are

commonly employed, which are based on the use of nickel generally dispersed

onto a high surface area support, such as for instance alumina or molecular sieves.

With these methods the impurity content can be reduced below one part per

billion (ppb, equivalent to one impurity molecule every 10^9 molecules of argon).

30   In these conditions it is also necessary to allow the control of the gas purity

and its constancy in time, for detecting increments of the impurity concentration,

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due for example to working anomalies of the purifiers, tightness losses of the gas lines or else.

A particularly interesting technique for carrying out this analysis is the ionization mobility spectrometry, also referred to in the field with the initials IMS (the same initials are also used for the instrument carrying out this technique, i.e. the "Ionization Mobility Spectrometer"). The interest for this technique derives from its very high sensibility, combined with the limited size and costs of the instrument; by operating in suitable conditions species in the gas or vapor phase can be detected in a gas medium in quantities of picograms (pg, i.e. 10^{-12} grams), or in concentrations of parts per trillion (ppt, equivalent to a molecule of the analyzed substance every 10^{12} molecules of the gas sample). IMS instruments and analysis methods in which these are employed are disclosed, for example, in US patents 5457316 and 5955886 in the name of the US company PCP Inc.

An IMS instrument is essentially made up of a reaction zone, a separation zone and a charged particles detector.

In the reaction zone the ionization of the sample comprising the gases or vapors to be analyzed in a transport gas takes place, commonly by means of beta-radiation emitted by ^{63}Ni. The ionization takes place mainly on the transport gas with the formation of the so-called "reagent ions", the charge of which is then distributed on the present species according to their electronic or proton affinities or to their ionization potentials. The book "Ion Mobility Spectrometry" by G. A. Eiceman and Z. Karpas, published in 1994 by CRC Press, can be referred to for an illustration of the (rather complex) charge transfer principles which are the base of the ionization mobility spectrometry technique.

The reaction zone is divided from the separation zone by a grid which, kept at a suitable voltage, prevents the ions produced in the reaction zone from entering into the separation zone. The moment in which the grid voltage is turned off, thus allowing the ions to enter the separation zone, is the "time zero" of the analysis. The separation zone comprises a series of electrodes which create an electric field such that the ions are carried from the reaction zone towards the detector. This zone is kept at atmospheric pressure: therefore, the motion speed of the ions

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depends on the electric field and on the cross-section thereof in the gaseous medium. By recording the current reading of the particle detector according to the time elapsed from the "time zero", peaks corresponding to the so-called "drift time" of the different present ions are obtained; by determining the drift time it is possible to go back to the presence of the substances object of the analysis.

In spite of its conceptual simplicity, the application of the technique involves some difficulties in the interpretation of the analysis results.

The instrument, analogously to chromatographs, provides as a result of the analysis the crossing times (drift times in the case of the IMS) of the ions corresponding to the present species, but it does not provide indications about the chemical nature of the ion corresponding to each peak.

For attributing each peak to a specific ion, the IMS may be connected to a mass spectrometer, which determinates the chemical nature of each ion, but in this way the above mentioned advantages of low cost and compactness are renounced.

Alternatively, it is possible to resort to calibration tests, wherein a sample formed of an extremely pure transport gas containing the substance object of the analysis is used, and the drift time of this latter is determined. The analysis in real conditions is however complicated since the various ionic species which are present may lead to phenomena of charge transfer with each other or with present neutral molecules, so that the determined drift times can be the characteristic times of species different from those, the presence of which has to be determined.

A possible method for overcoming the problems found in the real analyses consists in adding the sample gas with a specific substance, called "doping gas", which, according to various mechanisms, obtains the effect of notably decreasing the sensibility of the measure towards the species differing from the one which is the object of the analysis. As examples of practical application of the method of the doping gas may be mentioned US 4551624 relating to the addition of ketones or halogenated gases to the gas to be analyzed, US 5032721 and US 5095206 relating, respectively, to the use of phenols and sulfur dioxide in the analysis of acid gases, and US 5238199, relating to the use of amines in the analysis of chlorine dioxide. However, the doping gas method disadvantageously requires

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that a tank of this gas and means for its dosage in the gaseous medium are added to the system, thus leading to a complication of the measuring system based on the IMS instrument.

In the methods not based on the employment of a doping gas the possibility of carrying out a quantitative analysis is bound to the presence of a reactant ion. As previously described, the reactant ion generally is an ion corresponding to the gas present in higher amount in the mixture. Then, the reactant ion formed in the ionization zone transfers the charge to the other present species according to complex chemical balances. When the impurities concentration increases, also the charge quantity transferred thereto from the reactant ion increases, until the latter runs out. In the IMS spectrum this mechanism is reflected by the intensity increase of the peaks relevant to the impurities and by the simultaneous intensity decrease of the peak of the reactant ion, commonly defined in the field "Reactant Ion Peak" or RIP, up to its extinction. Obviously, when this condition is reached, the concentration of the ions relating to the impurities and the intensity of the relevant peaks in the spectrum do not grow any more also if the effective impurity concentration increases and therefore it is not possible any more to carry out a quantitative IMS analysis in this way. In the presence of water in argon, the RIP runs out with concentrations of about 10-15 ppb; thus, at the state of the art, this value is the maximum measure limit of this impurity in argon with the IMS technique.

It is therefore an object of the present invention to provide a method which is free from said disadvantages, i.e. a method allowing to measure water concentrations greater than 15 ppb. This object is achieved with a method, the main features of which are disclosed in the first claim and other features are disclosed in the subsequent claims.

Thanks to the calculation of the ratio between the intensities of the peaks detected at determined time positions in the signal coming from an IMS instrument, the method according to the present invention allows to precisely measure water concentrations in argon up to at least 30 ppb; the measurement of the peak intensity in the practice generally consists into the measurement of their

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area.

Furthermore, the method according to the present invention, when applied to the ultra-pure argon employed in the semiconductor industry (such as hydrogen, nitrogen and helium), does not require either doping gases or gas

5   purification processes before the IMS analysis, except when the same gas has impurities in relatively high concentrations, generally greater than about 10 ppb for each impurity.

According to a particular aspect of the invention, the calculation of the water concentration can be carried out in an automatic manner by using a

10   logarithmic formula which can be easily implemented in electronic calculation means, for instance in a personal computer.

Further advantages and features of the method according to the present invention will become clear to those skilled in the art from the following detailed and non-limiting description of an embodiment thereof with reference to the

15   attached drawings, wherein:

-   figure 1 shows a schematic view of the instrument carrying out the method according to the present invention;

-   figure 2 shows some spectrums obtained through the instrument of figure 1; and

20   -   figure 3 shows some test diagrams of the instrument of figure 1.

Referring to figure 1, it is seen that an IMS instrument 10 comprises in a known way a reaction zone 11 and a separation zone 12, which are divided by a grid 13. The gases let into the reaction zone 11 are ionized by means of a radiation source (not shown in the figure), for instance ^{63}Ni. The so produced ions are

25   guided into the separation zone 12 where, by means of electrodes (not shown in the figure) suitably arranged along the walls of the same zone, are accelerated toward an ion detector 14. The ions motion in the separation zone 12 is schematized in the figure by the arrows. The gas to be analyzed is let into the IMS instrument 10 through an inlet duct 15. The motion speed toward the ion detector

30   14 is slowed down by the presence of a counter-current flow of pure argon in the zone 12. For this purpose the IMS instrument 10 comprises at least one duct 16

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for introducing argon in the separation zone 12 from the side of detector 14. The latter is connected to a converter 17 which transforms the progress during the time of the electric signal of detector 14 into an analog or digital signal which can be displayed in turn on a display and/or a printer 18 by means of a spectrum 19

5   representing the result of the analysis.

Ducts 15 and 16 are preferably made up according the usual techniques of the pure gas technology, which generally involve the use of electropolished steel pipes for ensuring extremely limited degassing from the internal walls of the same ducts.

10   According to the invention, the gas to be analyzed is introduced into the reaction zone 11 of the IMS instrument 10 and analyzed according the typical way of this technique, i.e. by employing in the separation zone 12 of the IMS instrument 10 a counter-flow of a gas which does not interfere with the measurement, in particular argon; as it will be described in detail later on, the

15   position in the spectrum (in milliseconds, ms) of the peak due to argon, i.e. of the RIP, is known by the by knowledge of the test parameters; when the measuring system detects the RIP extinction, two peaks corresponding to two different ionic species relating to water are sought; by comparing the intensities of these two peaks, the water concentration in argon is calculated, in particular by means of a

20   logarithmic formula.

The position of the RIP, so as any other peak in an IMS spectrum, depends on the physical parameters with which the analysis is carried out. In particular, the most important parameter is the temperature of the gas in the separation zone: considerable temperature changes with respect to a reference temperature may

25   change the ratios between the time position of various peaks in the spectrum, thereby making the analysis impossible. A second important parameter is the ratio between the applied electric field and the gas pressure in the separation zone; changes of this ratio cause proportional changes of the positions of all the peaks in the spectrum, so that the spectrum is "compressed" or "expanded", although the

30   ratios between of the various peak positions are kept. Anyway, for convenience, it is preferable that the drift times remain fixed, for facilitating the identification of

the different peaks. Finally, the spectrum is influenced by the ratio between the mass flow of gas to be analyzed and mass flow of the counter-current gas, even if in lower measure with respect to the previous parameters. The two peaks relating to water, which are important for the method according to the invention, are the peaks corresponding to H_3O^+ and $(H_2O)_2^+$ ions. Therefore, for knowing the time position of these two peaks, it is necessary to carry out an IMS guiding test in the same conditions of the real analysis, with a water content in argon such that the RIP is not extinct. A complete spectrum is thus obtained: the presence of the RIP allows to assign the other peaks to the corresponding species, this correspondence being kept in the real analysis (without RIP).

EXAMPLE

The invention will be further explained by the following example, relating to a series of tests of water analysis with different concentrations in argon. In all the tests, the gas mixture flowing into the IMS instrument 10 is kept equal to 0,5 liters per minute and the gas temperature is 110 °C. The sample ionization is carried out by a ^{63}Ni radioactive source. The so generated ions are neutralized onto grid 13 until the voltage of the latter is canceled, thereby allowing their entrance into the separation zone 12. The cancellation time of the grid voltage is 200 microseconds (μs) for each test. The tests are carried out with an IMS instrument 10 wherein the separation zone 12 is 8 cm long; in every test the acceleration electric field is equal to 128 V/cm. From preliminary guiding tests it resulted that in these conditions the typical drift times of the species present in the tests are generally comprised between 15 and 30 milliseconds (ms); moreover, with a suitable test it has been determined that in these conditions the peaks of H_3O^+ and $(H_2O)_2^+$ are comprised between 15, 5 and 17 ms and between 17 and 19 ms, respectively (with maximums at about 16 and 17,8 ms, respectively). The results of all the tests are reported in spectrums 19 wherein the peaks have an area proportional to the concentration of a given ion according to the drift time of the same. The peak intensity is expressed in volts (V), while the current directly measured by detector 14 (number of ions colliding onto the detector per time unit) is transformed in volts by converter 17. The counter-flow of pure argon coming

from duct 16 has a rate of 2 liters per minute. Generally, the ratio between the flow rate of the gas to be analyzed and the counter-flow of pure argon can vary between 1:10 and 1:1.

Figure 2 shows a plurality of overlapping spectrums obtained by analyzing with the IMS instrument 10 a corresponding plurality of mixtures of water, argon and very little impurities, wherein only the water concentration changes. Along the axis of abscissas is shown the drift time of the ions in milliseconds, while along the axis of ordinates is shown a value proportional to the intensity of the signal emitted by the ion detector 14, for instance a voltage expressed in volts. The numbers inside the diagram distinguish instead the different spectrums according to the water concentration expressed in ppb present in the gas let into the IMS instrument 10.

As it can be noticed, without the presence of water, i.e. with 0 ppb of water, the relevant spectrum (shown with a bold line) has 4 peaks A, C, D and E, the latter of which is the tallest. The latter peak E, which in the conditions of the present test is in the time interval comprised between 23 and 25 ms, corresponds to the peak of the Ar^+ ions, i.e. to the RIP, while the other peaks A, C and D, comprised in the time intervals between 15,5 ms and 17 ms, 19 and 21 ms, and 21 and 23 ms, respectively, correspond to the ions of the impurities present in the gas mixture. In particular, the peak in the first time interval A is caused by the ions of H_3O^+, the second peak C is caused by the ions of the impurities and the third peak D by the ions of H_2O^+. The ions of H_2O^+ and H_3O^+ of peaks A and D are due to very small water concentrations which cannot be eliminated from the incoming gas mixture.

By increasing to 5 ppb the water concentration in the gas mixture and by keeping unchanged the other variables of the test, it can be noticed how the heights of peaks C and E notably fall, so as also the height of peak D is slightly reduced, while the height of peak A grows. Further, in the time interval between 17 and 19 ms a new peak B which is caused by the $(H_2O)_2^+$ ions can be distinguished. At 5 ppb peaks A and B have heights similar to each other and in any case higher than the remaining peaks C, D, and E.

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By increasing the water concentration in the mixture from 5 ppb to about 30 ppb, the height of peak B grows, while the height of peak A falls and peaks C, D and E substantially disappear. In particular, at around 18 ppb of water the height of peak A is equal to the height of the same peak with 0 ppb of water.

By further increasing the water concentration in the mixture beyond 30 ppb, the system is saturated and only peak B remains with a constant height.

As already said, the positions of peaks A and B were previously determined with a guiding test, thereby resulting in the time intervals between 15,5 and 17 ms and between 17 and 19 ms. By evaluating the intensity of these peaks, and in particular their area, the corresponding levels of the signal measured by the ion detector 14 are obtained. The water concentration contained in the analyzed gas can be determined by comparing said levels. In particular, for water concentrations lower than 30 ppb, it has been discovered that said comparison can be expressed with the following formula:

$$ppb_{H2O} = K \ln ((HB + HA) / HA), \text{ wherein:}$$

- ppb_{H2O} is the water concentration,
- K is a positive constant,
- HA is the area of peak A, and
- HB is the area of peak B.

Figure 3 shows a graph comprising the change during the time (abscissas) of two overlapping diagrams of the water concentration (ordinates). The first diagram, made up of a continuous line, shows the water concentration effectively present in a reference mixture let into the IMS instrument 10, while the second diagram, made up of a dotted line, shows the water concentration measured by means of the above described method. As it can be noticed, the trend of the second diagram substantially follows the trend of the first diagram up to 30 ppb, while differs beyond this concentration, in which the instrument is saturated.

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CLAIMS

1.   A method for measuring by means of ionization mobility spectrometry the concentration of water in argon, hydrogen, nitrogen and helium, characterized by comprising the followings operative steps:

- introducing the gas mixture to be analyzed into an IMS instrument (10) with a counter-flow of pure gas;

- obtaining a signal (19) variable during the time and proportional to the number of ions detected by an ion detector (14) of the IMS instrument (10);

- determining two time intervals (A, B) corresponding to the drift times in the IMS instrument (10) of the H_3O^+ and $(H_2O)_2^+$ ions present in the gas mixture;

- obtaining the peaks of said signal (19) in the two determined time intervals (A, B);

- calculating the water concentration in the gas mixture according to the ratio between the intensity of the two peaks obtained in the signal (19).

2.   A method according to claim 1, characterized in that the water concentration in the analyzed gas is calculated by means of the following formula:

ppb_{H2O} = K ln ((HB + HA) / HA), wherein:

- ppb_{H2O} is the water concentration in ppb,

- K is a positive constant,

- HA is the intensity of the peak of the signal (19) in the time interval (A) corresponding to the drift times of the H_3O^+ ions in the IMS instrument (10); and

- HB is the intensity of the peak of the signal (19) in the time interval (B) corresponding to the drift times of the $(H_2O)_2^+$ ions in the IMS instrument (10).

3.   A method according to claim 2, wherein the area of the peaks is employed as a measure of said intensity of the same.

4.   A method according to claim 2, wherein the height of the peaks is employed as a measure of said intensity of the same.

5.   A method according to one of the previous claims, characterized in
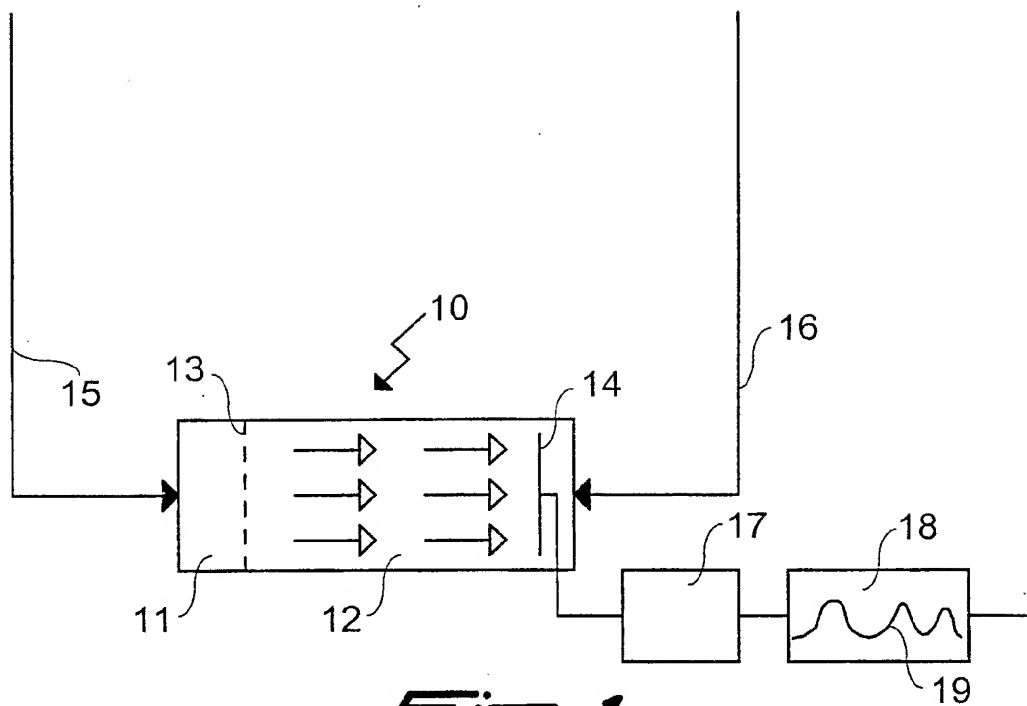
that the two time intervals (A, B) corresponding to the drift times of the H_3O^+ and $(H_2O)_2^+$ ions in the IMS instrument (10) are determined with a preliminary guiding test carried out with values of the operative parameters equal to those employed in the actual analysis.
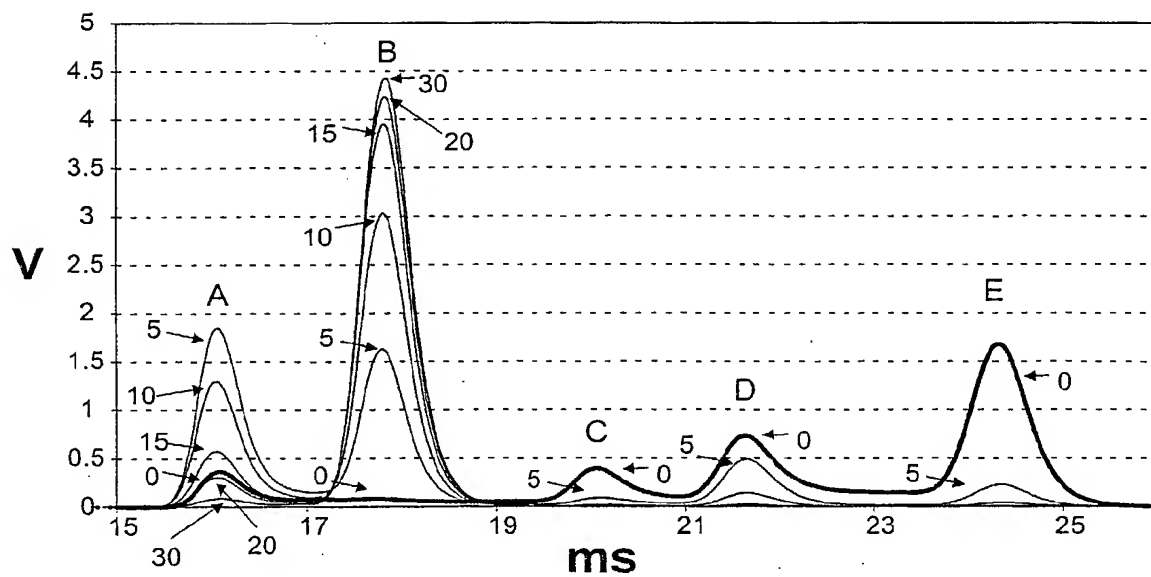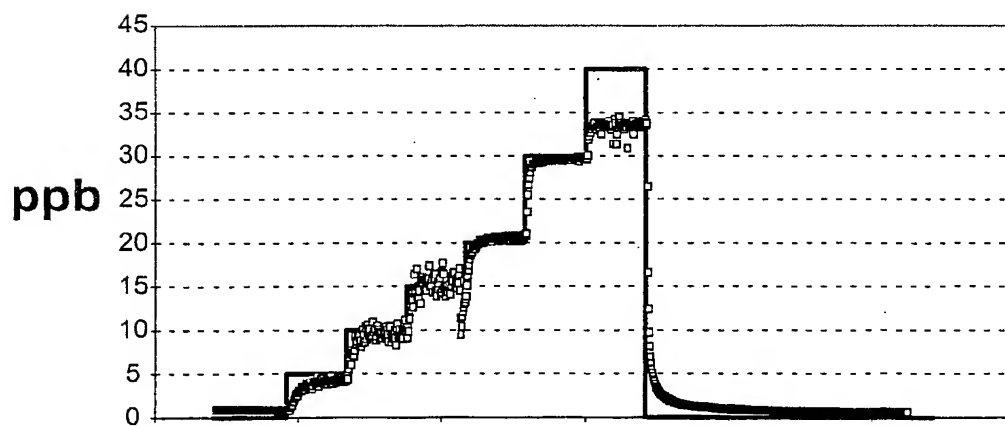
5   6.   A method according to claim 5, wherein said operative parameters comprise at least the temperature of the analyzed gas mixture.

7.   A method according to claim 6, wherein said operative parameters comprise also the electric field in the separation zone (12) of the IMS instrument (10).

10   8.   A method according to one of claims 5 to 7, characterized in that the analysis is carried out with gases at the temperature of 110 °C and with an electric field in the separation zone (12) of 128 V/cm, and the two time intervals (A, B) corresponding to the drift times of the H_3O^+ and $(H_2O)_2^+$ ions in the IMS instrument (10) are comprised between 15,5 and 17 ms (A) and between 17 and 15   19 ms (B).

Fig.1

Fig.2

Fig.3